NRL Report 7335

Characterization of Hot-Pressed MgO

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Chemistry Division

November 16, 1971

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Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Naval Research Laboratory Washington, D.C. 20390	Unclassified
	2b. GROUP

3. REPORT TITLE

CHARACTERIZATION OF HOT-PRESSED MgO

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on the NRL problem; work is continuing.

5. AUTHOR(S) *(First name, middle initial, last name)*

Roy W. Rice

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
November 16, 1971	34	51

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
NRL Problem C05-28	
b. PROJECT NO. RR 007-02-41-5677	NRL Report 7335
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Department of the Navy (Office of Naval Research), Arlington, Virginia 22217

13. ABSTRACT

Dense bodies of hot-pressed MgO are characterized for impurity or additive (LiF or NaF) contents and changes with subsequent annealing. As-hot-pressed bodies from a variety of raw materials and pressing techniques are shown by ir, mass spectrometry, and weight-loss measurements to contain variable amounts of hydroxides, carbonates, and possibly bicarbonates averaging several hundred parts per million in total content. The gases released in the decomposition of these impurities can cause clouding and bloating of bodies on annealing subsequent to hot-pressing, depending on concentration, specimen size and integrity, and heating rates.

The other predominate impurities, Ca and Si, are observed primarily along triple lines in large grain specimens (i.e., those with substantial annealing after hot pressing). Some of these impurities are also found on grain boundaries in patches much smaller than the grain size. In finer grain-size bodies, much of the Ca and Si also appears to be along triple lines, but some is present as patches that appear to follow grain boundaries over an area of several grains. The size and distribution of these patches are quite irregular. Since the Ca may initially be present as the hydroxide and carbonate, its inhomogeneity may be related to that of the above anion impurities.

Most of the Li and Na which were added as fluorides is lost during hot-pressing. More F than Li or Na remains, indicating that it reacts with MgO. Li, Na, and F contents are all further reduced by subsequent annealing, so that only a few hundred parts per million F are retained in smaller bodies after moderate annealing. Differences in specimen colors for various materials and fabrication methods and changes in color with annealing indicate interaction of additives with impurities and differences in amount or association of impurities. Differences in association or amount of impurities are also indicated by marked changes in surface hydration of some MgO bodies after annealing and by different impurity structures formed on annealed surfaces in other bodies. Surface scratches are shown to be removed by annealing at or below 1500°C. (Continues)

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ceramics						
MgO						
Hot-pressing						
Impurities						
Anion impurities						
Characterization						
Imperfections						
Grain growth						
Porosity						
Surface						
Hot-pressing additives						
Pressure calsintering						
Fabrication						

Grain growth data are presented for dense bodies and bodies with a low percent of porosity. Pores in fine-grain bodies are small and predominantly at the grain boundaries. With further grain growth, the pores grow and become located mostly within the grains, approximately as negative crystals.

CONTENTS

ABSTRACT

Three methods of hot-pressing dense MgO bodies are described. Two of these methods start with MgO powders, one using LiF or NaF additions, and the other, no additions. The third method involves the direct hot-pressing of precursor salts (e.g., $Mg(OH)_2$). The latter two methods use temperatures of approximately 1300°C with pressures of 5000 psi for times of about 15 minutes to assure complete densification. The addition of LiF lowered the pressing temperatures 300° to 400°C, and the addition of NaF, 200° to 300°C. Hot-pressing problems and imperfections in the resulting bodies are discussed to aid in further improvement. The most fundamental problem was removal of the gaseous impurities such as H_2O and CO_2 from the powders. Vacuum-hot-pressing aided some but did not completely remove them. Explosions and lenticular voids are major problems attributed to these gaseous impurities. Other impurity effects on color, most likely due to cation ion purities, are also noted. Densification mechanisms are discussed, and the possible effects of gaseous impurities in hot-pressing mechanisms with or without additives are noted. The main effect of hot-pressing with NaF or LiF may be primarily to bring about more intimate contact between particles by enhanced interparticle sliding. The actual sintering mechanism which occurs whether or not pressure is applied is probably diffusion in the region of the grain boundary due to retained fluoride, most likely as a liquid phase.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem C05-28
Project RR 007-02-41-5677

Manuscript submitted July 23, 1971.

CHARACTERIZATION OF HOT-PRESSED MgO

INTRODUCTION

The purpose of this report is to provide further data to improve the interpretation of MgO hot-pressing and to provide the basis for a more detailed interpretation of the strength and fracture of hot-pressed MgO (1). A central focus of this analysis will be changes in hot-pressed MgO with subsequent annealing, making note of poor as well as good specimens. It is important to note these changes since grain growth is not the only result of annealing at higher temperatures. Failure to detect these changes has probably been a major factor in the varying interpretations of the behavior of MgO. The materials investigated cover raw materials used in most investigations of the hot-pressing and properties of MgO (Table 1).

EXPERIMENTAL TECHNIQUES

Primarily the hot-pressed bodies described in Ref. 10 were analyzed, especially bodies from F and M MgO powder (Ref. 1 and Table 2); these analyses are shown in Table 3. Also analyzed were specimens supplied by Morgan (23, 24) of Cornell University (herein designated C MgO) and specimens supplied by Leipold of the Jet Propulsion Laboratory (herein designated JPL MgO). Leipold supplied both F MgO and high-purity MgO samples; both types were hot-pressed in metal or Al_2O_3 dies.

All annealing was in air unless otherwise noted, using a silicon carbide resistance-heated furnace to 1650°C and a ZrO_2-lined furnace using excess oxygen with natural gas above 1650°C. All specimens were annealed resting on edge near their ends on MgO crystals with 99% pure MgO crucibles as muffles. In annealing below 1650°C, recrystallized alumina trays were used as an intermediate container between the MgO crucibles and MgO crystals. Annealings in other atmospheres were carried out in a mullite tube furnace.

Most analytical techniques and equipment have been previously described (10,26). All optical transmission studies, including ir analysis, were done on solid samples. Normal transmission from 3.0 microns to 0.2 micron was measured on a Beckman DK-2A spectrophotometer. F content was analyzed by a radiochemical extraction technique using Ta^{182} (27,28), which compared well with a neutron activation analysis. Mass spectrometer data were obtained by heating solid samples (about 1 gram) in a tungsten crucible in a Knudsen cell. Heating to 2000° to 2200°C was accomplished in 4 to 7 hours after an initial overnight pumpdown.

Bars about 0.1 by 0.25 in. in cross section were used for several tests. Grain size (linear intercept) was obtained (usually near the tensile surface) from fracture surfaces of such bars broken in flexure. Electron micrographs were used to determine most grain sizes below 10 microns, and exclusively for those below 4 microns. Electron probe examination of specimens was as previously described (16). Some of the optically examined fractures were partially polished if they were too rough. Some specimens were etched using boiling chromic acid (2.5 g CrO_3 per 10 cc H_2O) (11,12). Fracture surfaces were etched 3 to 15 sec (normally about 5 sec) and sanded surfaces 15 to 100 sec (normally about 30 sec).

Note: This work was done while the author was employed in the Space Division of The Boeing Co., Seattle, Wash.

Table 1
Source of MgO Powder Used in Other Studies

Investigator	Reference	Study
A. Investigators using Fisher Electronic Grade MgO		
Spriggs and Vasilos	2	Mechanical properties
Vasilos et al.	3	Mechanical properties
Passmore et al.	4	Creep
Spriggs et al.	5	Grain growth
Leipold and Nielsen	6	Fabrication
Leipold	7	Impurity distribution
Copley and Pask	8	Mechanical properties (e.g., material from Spriggs)
Day and Stokes	9	Mechanical properties (e.g., material from Spriggs)
Rice	1,10,11,12	Fabrication and mechanical properties
Rice et al.	13	Hot extrusion, strength, and fracture
Spriggs et al.	14	Fabrication
Vasilos and Spriggs	15	Fabrication
Rice and Racus	16	Impurity distribution
Chung et al.	17	Elastic moduli
Soga and Anderson	18	Elastic properties
B. Investigators using Mallinckrodt AR MgO		
Hanna	19	Infrared properties
Hanna	20	Fabrication
Tagai and Zisner	21	Creep
Rice	1,10,11,12	Fabrication and mechanical properties
Rice et al.	13	Hot extrusion and mechanical properties
Day and Stokes	9	Mechanical properties (e.g., material from Rice)
Morgan and Schaeffer	22	Fabrication
Chung et al.	17	Elastic moduli

Table 2
Designation of Bodies from Various Powder Sources

Designation	Raw Material or Specimen Source
F	Fisher Electronic Grade (M-300) MgO
M	Mallinckrodt analytical-reagent-grade MgO
G	E. Merck reagent MgO
MBC	Mallinckrodt Magnesium Basic Carbonate
DH	Dow Chemical Company $Mg(OH)_2$
FH	Fisher reagent-grade $Mg(OH)_2$
C	Pressure calsintered MgO from P. Morgan
JPL	High-purity hot-pressed MgO from M. Leipold (25)

Note: Reference 25 gives further details.

Table 3
Impurity Analysis of MgO Powders*

	Fisher Electronic Grade, Low Activity, Reagent MgO† Typical Impurity Content‡	Mallinckrodt Analytical Reagent MgO† Maximum Limits of Impurities‡
	Weight — Percent	
Ignition loss	1.6	2.0
Soluble in H_2O	0.55	0.40
Insoluble in HCl	0.09	0.020
NH_4 precipitate	0.005	0.020
SiO_2	0.10	0.040
S	0.013	0.005
Cl^-	Trace	0.010
NO_3^+	None	0.005
Ba	None	0.005
B	Trace	Not listed
Ca	0.01	0.05
Cu	Trace	Not listed
Fe	0.03	0.01
Mn	None	0.0005
K	Not listed	0.005
Na	None	0.5
Ag	Trace	Not listed
Sr	Not listed	0.005
Ti	None	Not listed
Va	Trace	Not listed
Zn	None	Not listed
Heavy metals (as Pb)	Not listed	0.003

*Manufacturer's data.
†Manufacturer's designation.
‡Type of analysis.

EXPERIMENTAL RESULTS

Changes in Appearance with Annealing

Color Changes

Changes in appearance, as seen with the unaided eye, are presented first since they often offer clues to microstructural and chemical changes, which will be presented later, and because some of them are very important. All specimens changed color with annealing subsequent to hot-pressing (Fig. 1). M MgO fabricated with NaF behaved similar to that made with LiF. The brown-to-black translucent glossy color that developed on annealing M MgO was often absent at or near the less dense surface and was darkest in the center, where it disappeared last. Specimens directly hot-pressed from MBC powders similarly turned black in areas that had been translucent as-hot-pressed.

G MgO specimens vacuum-hot-pressed at lower temperatures (1260°C) turned black inside like M Mgo on annealing, but not those hot-pressed at higher temperatures (1315°C), which were dark gray as-hot-pressed especially on the central area. All specimens lost this brown or black color on annealing to 1400° to 1600°C in air. In low-temperature

MATERIAL	AS HOT PRESSED COLOR	COLOR DESCRIPTION[1,2]
M MgO	Very slightly gray	← Becoming brown to black → ← Becoming white or clear →
M MgO with LiF	Usually light gray	← Becoming white or clear → ← White or Clear →
M MgO + 1 w/o Al_2O_3 with LiF	Usually light gray	← Becoming white or clear → ← White or Clear →
F MgO	Usually light gray or blue	← Loosing gray → ← Yellow to Brown → ← Getting light yellow tint →
F MgO with LiF	Usually light gray	← Becoming light pink → ← Light Pink →
F MgO + 2-5 w/o CaO	Gray	← Becoming White → ← White →
F MgO + 2-5 w/o CaO with LiF	Gray	← Becoming light pink → ← Light Pink →

900 1000 1100 1200 1300 1400 1500

After Air Firing at: Temperature, °C

(1) Based on changes in specimens typically 0.1-0.15" in thickness and 0.15-0.3" in width, after cooled to room temperature.

(2) White or clear refers to colorless if transparent and white if only poorly translucent.

Fig. 1 - Firing color changes

annealing or quenchings, light orange or orange-pink colors also developed in some of the M MgO-LiF specimens. The quenching colors were not obtained if specimens were annealed to about 1150°C or more. Specimens of any MgO that had been a dull, opaque black as-hot-pressed (2) turned white or clear progressively in from the surface, to depths of about 0.1 in. or more after air annealing to about 1150°C.

Transparency, Clouding, Blistering, and Bloating

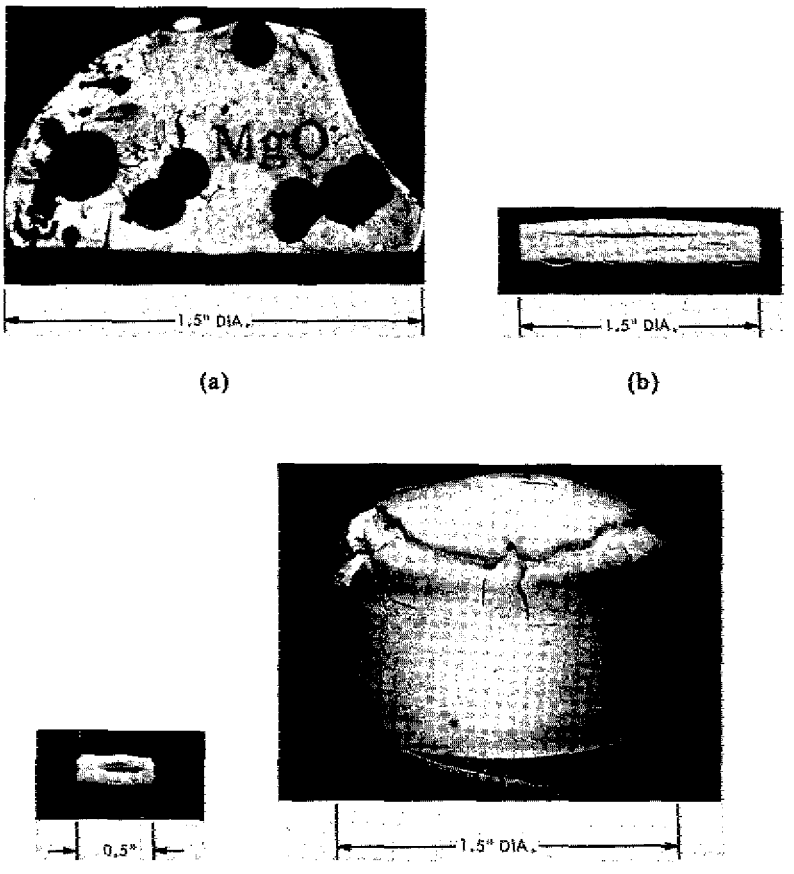
Translucency or opacity after hot-pressing was no guarantee of these same properties after subsequent annealing. A few black, and several gray, opaque hot-pressed specimens became translucent or transparent on air annealing. Many translucent specimens improved on firing, but many were degraded. Development, or growth, of lenticular pores, often in a transparent matrix (Fig. 2a), was a common degradation. When these occurred near the surface, they bulged above the surface, forming "blisters" (Fig. 2b) when temperatures or additives (e.g., LiF) allowed the necessary creep-plasticity. Though they most commonly formed perpendicular to the pressing direction, many did not; sometimes they formed on all surfaces of rectangular blocks cut from pressings and on the sides of cylindrical pressings. The extreme of this blistering problem was often a gross bloating (Figs. 2b, 2c, 2d, and 3), even of large cylinders. During annealing, thin laminar blisters also frequently formed in hot-pressed bodies over parts of interfaces between previous successive cold-pressed layers, thus more clearly showing such interfaces.

Clouding (loss of translucency or transparency) was also a frequent problem. It was most commonly observed inside a translucent or transparent surface layer (Fig. 3), but it sometimes extended throughout the entire specimen, especially in blistered or bloated specimens where it usually was most severe (Figs. 2b and 2c).

Despite many variations in annealing results, some general body, material, and firing parameters were found. The important body parameter was thickness. Transparency generally decreased with increasing thickness, usually by clouding inside a transparent surface layer. Fairly uniform transparency could be achieved in some specimens up to about 0.35 in. thickness (primarily those made with LiF), but not in bodies 0.75 in. or more in thickness, the best of which showed more transparency on the surface than inside. Thickness of the piece being annealed was most important since thin (about 0.1 to 0.2 in. thick) slabs cut from the central area of thick hot-pressings were often transparent, while thicker pieces from the same pressing usually had cloudy cores. Bloating and blistering were more common in thicker bodies.

Annealing of F and M MgO hot-pressed with LiF gave the most consistent and uniform transparency, with 0.5-, 1.0-, and 2.0-w/o additions generally giving progressively better results. Bodies of F MgO made without additives were more prone to clouding on annealing, but some produced uniform transparent specimens. Annealing of M MgO without additives generally gave less transparency than F M MgO with the transparent areas often being irregular in shape and generally not extending to the edges of the pressed disk. However, some transparent areas of annealed M MgO were often among the clearest in any specimen (after the brown-black color disappeared). Specimens that were a dull black as-hot-pressed tended to cloud on annealing.

The JPL high-purity MgO varied from little to substantial clouding, with the clouding being fairly uniform across a piece that had a uniform degree of translucency (high or low) to start with. Clear sections of the JPL F MgO clouded inside, but retained a clear surface. C MgO clouded some, and some thin blisters in it expanded. Specimens directly hot-pressed from the DH (hydroxide) powder clouded substantially, while those from FH clouded very little. G MgO samples that did not turn black tended to cloud some. Defects in annealed bodies generally corresponded to problems encountered during hot-pressing (2), but were much more extreme and consistent. Thus, while some lots gave



(a) (b)

(c) (d)

Fig. 2 - Severe blistering of dense MgO on annealing. (a) Thin lenticular "voids" or blisters (dark circles) inside of body. Note transparency shown by the letters MgO showing through specimen. (b) and (c) Translucent bodies that clouded (became opaque) on annealing and developed blisters as well as some general bloating (swelling). All specimens were M MgO hot-pressed with 2-w/o LiF. (d) M MgO plus 5-w/o NiO hot-pressed with 2-w/o LiF then fired to about 1300°C. Bodies with NiO showed greater extremes of such bloating, but severe problems were also observed in MgO made with or without LiF.

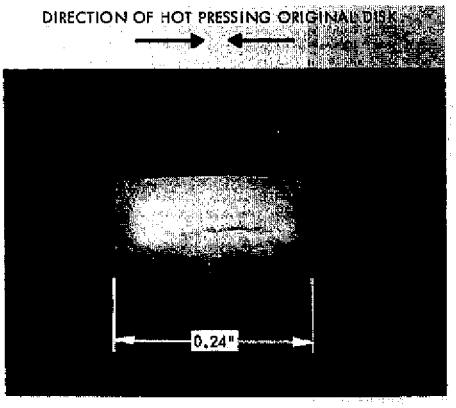


Fig. 3 - Cloudy core in a transparent periphery. Note some bloating as shown by curved sides (flat before annealing) and the central "void" that developed. Specimen was from an F MgO disk vacuum hot-pressed without additives. It was somewhat transparent as-hot-pressed. The surface increased in transparency, and the central clouding and bloating occurred during heating from about 800°C to 1500°C for 1 hour in air.

less frequent translucency on hot-pressing, these same lots gave consistent clouding on annealing. Similarly, clouding was more prevalent in powder open to the air for longer periods prior to use. However, powders exposed to 100% relative humidity at 100°F (40°C) for varying times up to 1 month showed no consistent differences.

Problems of clouding, bloating, and blistering were generally not observed until annealing temperatures of about 800°C or more were reached. Heating rates in the first few hundred degrees did not appear to affect the annealing results; however, beyond this range, slow heating rates (approximately 15°C/hour) improved the number and quality of translucent to transparent specimens. Fast heating (50°C/hour or more) clouded many more, but not all, specimens. Annealing of specimens close together or sandwiched between MgO crystal slabs appeared to reduce the frequency and degree of transparency, while providing a free surface and/or circulation around each specimen appeared to improve results, especially for specimens made with LiF or NaF. Once annealed to about 1100°C to 1200°C, transparent specimens (at least thin ones) were likely to remain so under any further annealing conditions. Using these techniques, about 20% of the specimens or more were transparent. Though none were completely transparent, some approached this state as shown in Fig. 4. Less than 20% of thinner (0.1-0.2 in.) specimens were opaque, and severe blistering and bloating were fairly limited in frequency.

Surface Changes

All dense as-hot-pressed pieces of MgO showed very limited hydration, forming a very thin surface film usually noticeable only after many months, about the same as MgO crystals. However, F MgO hot-pressed with or without LiF, when subsequently annealed to intermediate temperatures (1100°-1500°C), showed a marked increase in surface hydration, usually forming a much thicker, chalky-appearing coating in a few weeks. The coating would often flake off, especially from a well-polished surface. This generally did not occur on F MgO specimens chemically polished in boiling phosphoric acid and tended to decrease in severity and occurrence with air annealing beyond 1600°C. It was not observed with other MgO bodies.

Specimens made with LiF frequently showed a clear film suggestive of a solidified and crystallized liquid covering much of the surface on specimens annealed for only a short time at temperatures of about 1100°C or less.

Effects of Other Atmospheres

Limited annealing in argon and in nitrogen indicated that these gases did not give specimens as clear as air annealing. Cursory tests in hydrogen indicated that MgO remains

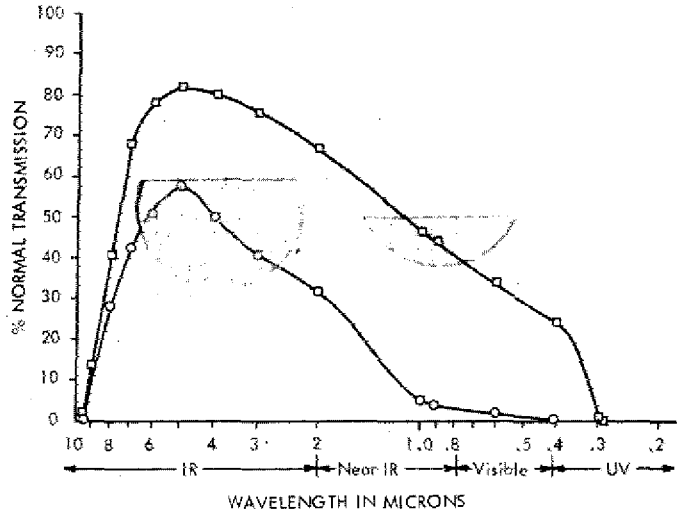


Fig. 4 - Transparency of hot-pressed MgO. M MgO was hot-pressed with 2-w/o LiF, then annealed to 1100°C in about 60 hours. Note the specimens (about 0.090 in. thick) on their respective curves.

grayer longer, but that some MgO made with LiF may become clearer than when annealed in air. Such hydrogen annealings clearly showed that the regions of M MgO (hot-pressed without additives) that become brown to black at intermediate temperatures in air become blue in hydrogen. The few pieces of F MgO hot-pressed with LiF fired in hydrogen never turned pink as did other pieces from the same pressing annealed in air.

Microstructural Changes

Bulk Changes

Grain growth data are shown in Figs. 5 and 6. F MgO hot-pressed with LiF, then annealed, generally resulted in larger grains than F MgO hot-pressed without LiF despite the generally larger starting grain size of the latter. Specimens made with NaF appeared to have an average grain growth intermediate between specimens made with and without LiF. However, all grains near the surface and some grains scattered inside this layer (300 to 500 microns thick at 1300°C) were several-fold larger than the other grains, with this layer thickening on annealing.

Annealing generally reduced porosity, especially in the most porous starting specimens. However, porosity along grain boundaries (Fig. 7) also appeared as a result of initial annealing in the range 800° to 1200°C, with the severity of this porosity generally increasing with the severity of clouding. Porosity in less dense hot-pressed specimens, or specimens that developed porosity (and thus clouding) at lower annealing temperatures, was generally fine and at grain boundaries, usually near or along triple lines. Most, or all, remaining porosity was within the grains, larger, and in the general form of negative crystals after annealing above 1400° to 1500°C.

Electron probe analysis of M and F MgO showed that Ca- and Si-rich impurities were fairly prevalent in both. With little or no annealing, these impurities were rather inhomogeneously distributed with substantial variation from pressing to pressing as well as within a given pressing. Their main concentration was usually in patches that appeared to be along grain boundaries. These patches were occasionally very large in comparison to the

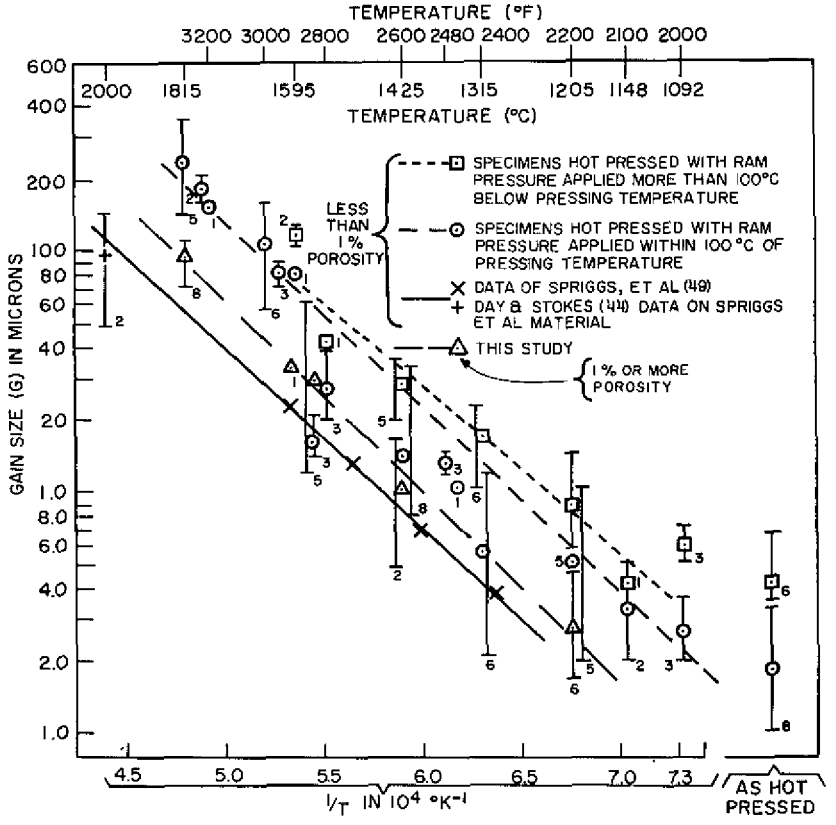


Fig. 5 - Grain growth of F MgO hot-pressed without additives. Specimens were annealed in air approximately 1 hour at the temperature after hot-pressing. Vertical bars represent the range of data and subscripts the number of specimens.

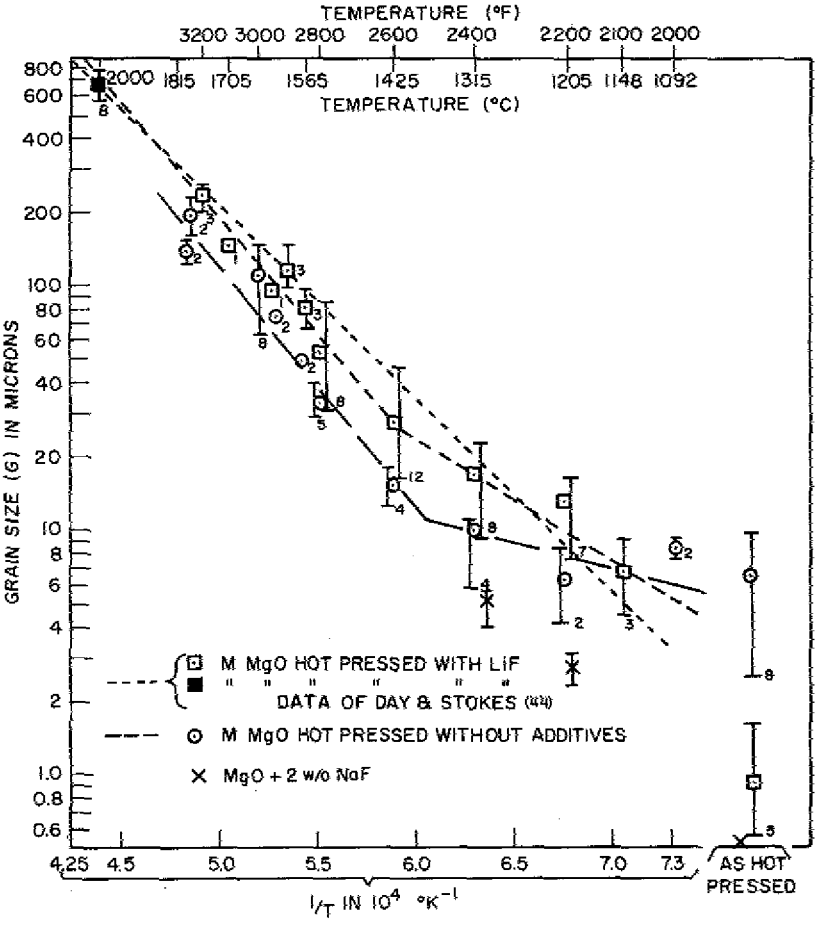
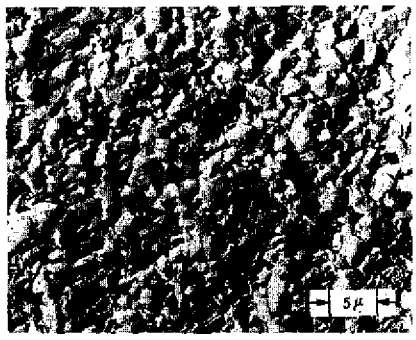
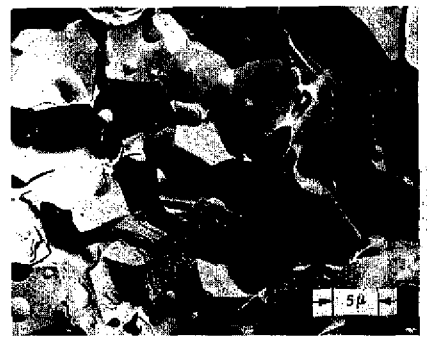


Fig. 6 - Grain growth of M MgO hot-pressed with and without LiF. Specimens were annealed in air approximately 1 hour at the temperature after hot-pressing. Vertical bars represent the range of data and subscripts the number of specimens. Specimens made without LiF indicate a change in grain growth rate; those made with LiF may also have a similar change in grain growth rate.



(a) Fine-grain specimen, which was not hot-pressed to full density. Note pores at triple points.



(b) A specimen that clouded on annealing with resultant pores on grain boundary surfaces

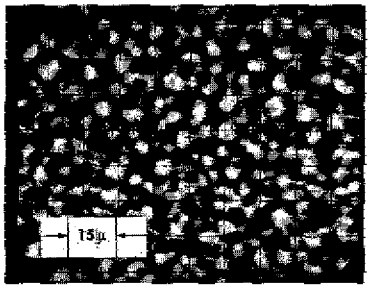
Fig. 7 - Porosity in finer-grain MgO

grain size (Fig. 8). However, electron micrographs, Fig. 9, generally showed an apparent second phase along triple lines, even with little or no annealing. In some electron micrographs, short stubby whiskers were seen along grain boundaries. On the other hand, large-grain specimens, i.e., those having been annealed to relatively high temperatures, typically had a more homogeneous impurity distribution, with most along triple lines and some in grain boundary patches much smaller than the grain size (Fig. 10). The transition to the larger-grain impurity distribution generally became fairly distinct after annealing to 1400° to 1500°C (generally giving 50- to 100-micron grain sizes). Ca and Si impurities were generally coincident, but Ca usually appeared in greater concentration, especially near the surface, at least in F MgO. Some Fe, especially in F MgO, was found, generally fairly homogeneously distributed. These results appear to be independent of whether or not additives were used.

Surface Changes

Surface scratches from sanding (600 grit finish) showed substantial rounding or elimination after slow annealings to 1100° to 1200°C and were well rounded or gone after 1200° to 1400°C, but thermal etching of grain boundaries became apparent at 1100° to 1200°C and quite clear at 1200° to 1400°C. These results were generally the same for F and M materials made with or without LiF; however, the accumulation of impurities on the surface was distinctly different. M MgO made with or without LiF generally developed rectangular protrusions (Fig. 11) on most surfaces, for example, those of cut bars, after air annealing to 1400° to 1500°C or more; LiF may have made their occurrence at lower temperatures more frequent. A thin-section analysis showed these to be optically anisotropic, while several probe tests showed they were rich in Ca and Si (generally more Ca). Such protrusions varied in number, size, and clustering over a given sample and from sample to sample but were almost exclusively absent from lower density areas such as the periphery of M MgO disks hot-pressed without additives. Dense F MgO also showed some Ca- and Si-rich objects on the surface. However, these were round or elongated (Fig. 12) and often appeared as depressions, suggestive of voids that have migrated to the surface with impurities.

A fairly thick surface layer of smaller grains was observed in most finer-grain-size bodies, obtained from little or no annealing. A similar situation sometimes occurred in larger-grain-size bodies, or those fired to higher temperature, Fig. 13. There were also occasionally exceptionally large surface grains in some specimens annealed to elevated temperatures.



(a) Specimen current presentation showing grain size and fracture topography (intergranular fracture at 2400° F)

(b) Ca x-ray fluorescence of same area. White patches are Ca rich.

Fig. 8 - Electron probe examination of finer-grain F MgO specimen (as-hot-pressed)

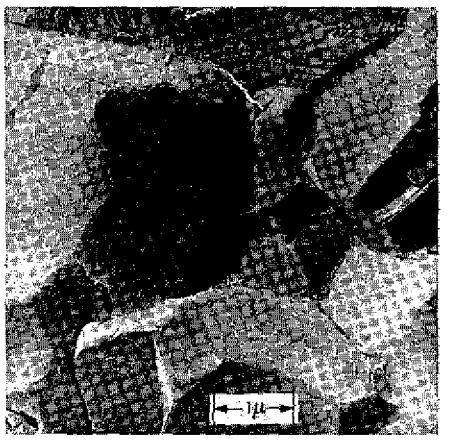
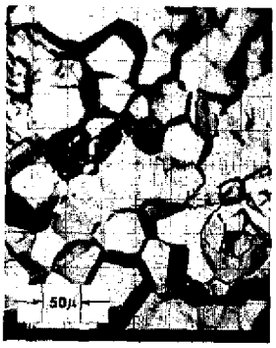
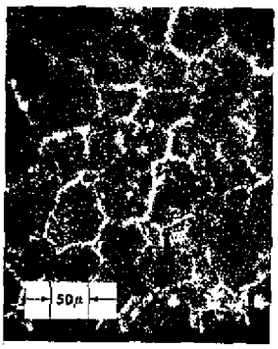


Fig. 9 - Electron micrograph showing probable second phase along triple lines

(a) Specimen current presentation showing fracture topography (*intergranular fracture at* 2400° F)





(b) Ca x-ray fluorescence of same area. White patches show Ca-rich areas.

(c) Si x-ray fluorescence of *same area.* White patches show Si-rich areas.

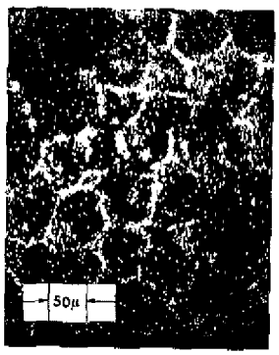


Fig. 10 - Electron probe examination of larger-grain MgO *specimen (annealed to 2960° F (1660° C)* for one hour)

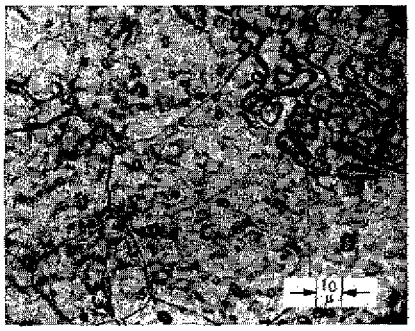


Fig. 11 - Rectangular protrusions on annealed surface of M MgO. Surface of specimen was annealed in air to 1540°C. Note the individual and clustered protrusions. Clusters occurred fairly frequently and were often several times the grain size.

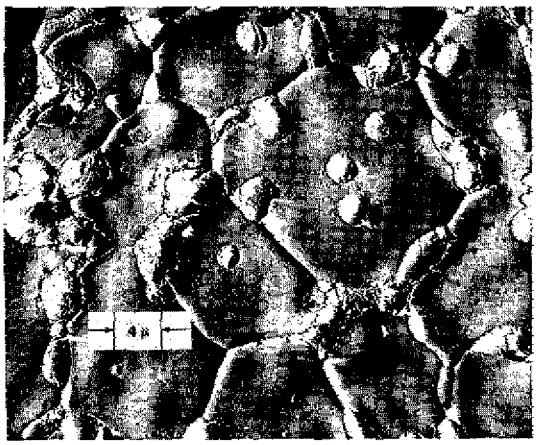
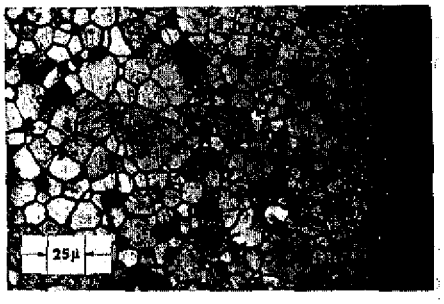
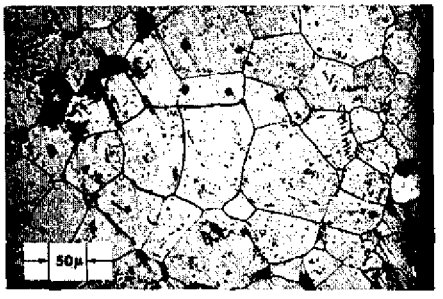


Fig. 12 - Electron micrograph of the surface of a hot-pressed F MgO specimen annealed to 2800°F (1540°C) for 1 hour. Electron microprobe analysis shows that the round and elongated structures are rich in Ca and Si.

(a) Specimen annealed to 2200°F (1205°C)





(b) Specimen annealed to 2800°F (1540°C)

(c) Specimen annealed to 3200°F (1760°C)

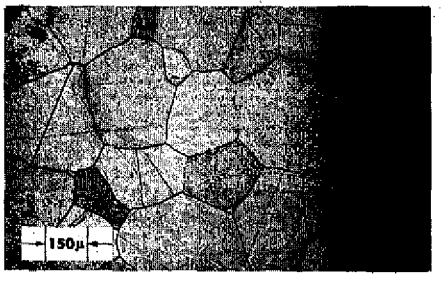


Fig. 13 - Smaller surface grains

Changes in Composition

Sodium, Lithium, and Fluorine Analysis

Residual fluoride analysis on some M MgO samples made with LiF and NaF are shown in Table 4.

An analysis by emission spectroscopy showed only trace amounts of Li left in a dense M MgO specimen (0.1 in. thick or less) after hot pressing with 2 w/o LiF. Such analysis of fragments about 0.25 in. or less in maximum dimension from another dense M MgO disk (about 0.15 in. thick) hot-pressed with LiF showed no trace of Li after being annealed to 2100°F (1150°C). Flame photometry analysis of two samples from the same disk of M MgO (the same disk as for specimens 6 and 8 in Table 4) hot-pressed with NaF showed 0.22 w/o Na in an as-hot-pressed piece and 0.01% in a piece annealed to 2400°F (1315°C).

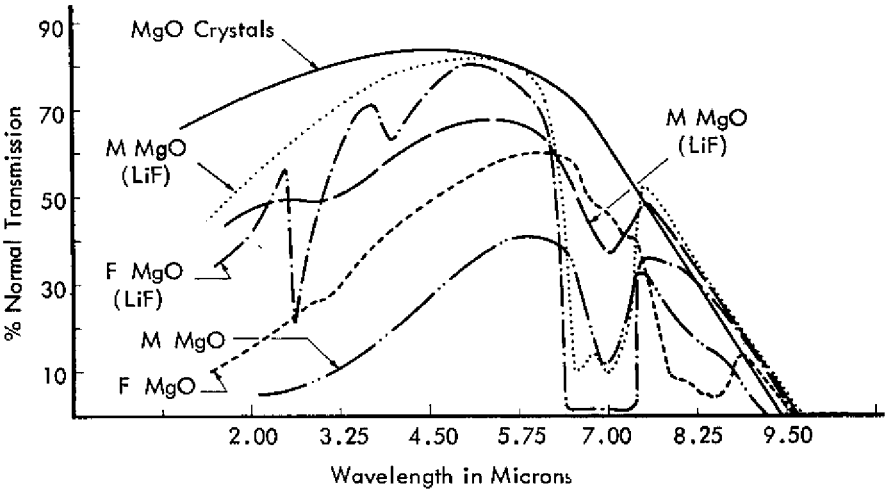
Infrared, Mass Spectrometer, and Weight-Loss Analysis

Infrared transmission tests of as-hot-pressed specimens consistently showed some absorption in a limited number of bands (Fig. 14). The degree of absorption in any or all bands

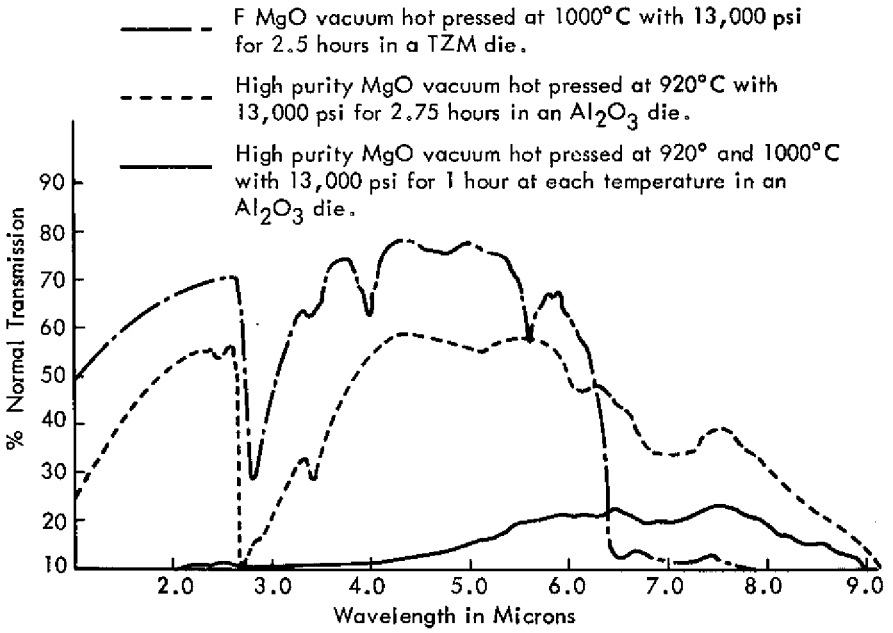
Table 4
Fluoride Analysis of Bodies Hot-Pressed With LiF or NaF

Sample No.	Material	Additive	Condition of Test Sample	Approximate Percent of Theoretical Density	Approximate Thickness (in.)	F Content (Wt.-%)
1	MgO	2 w/o LiF	As hot pressed	99	0.2	0.9
2	MgO	2 w/o LiF	Fired to 2400°F (1315°C)	99	0.2	0.08
3	MgO	2 w/o LiF	Fired to 2750°F (1510°C)	99	0.2	0.06
4	MgO	2 w/o LiF	Fired to 2400°F (1315°C)*	99	1.0	0.10
5	MgO	1 w/o LiF	Fired to 2600°F (1425°C)	99	0.1	0.005
6	MgO	2 w/o NaF	As hot pressed	97	0.1	0.45
7	MgO	2 w/o NaF	As hot pressed	97	0.1	0.65
8	MgO	2 w/o NaF	Fired to 2500°F (1370°C)†	97	0.1	Less than 0.04

*This sample subsequently was heated in a sealed tungsten can to 2150°C for 30 to 40 minutes and analyzed after this operation.
†This sample and sample 6 are from the same hot-pressed disk.

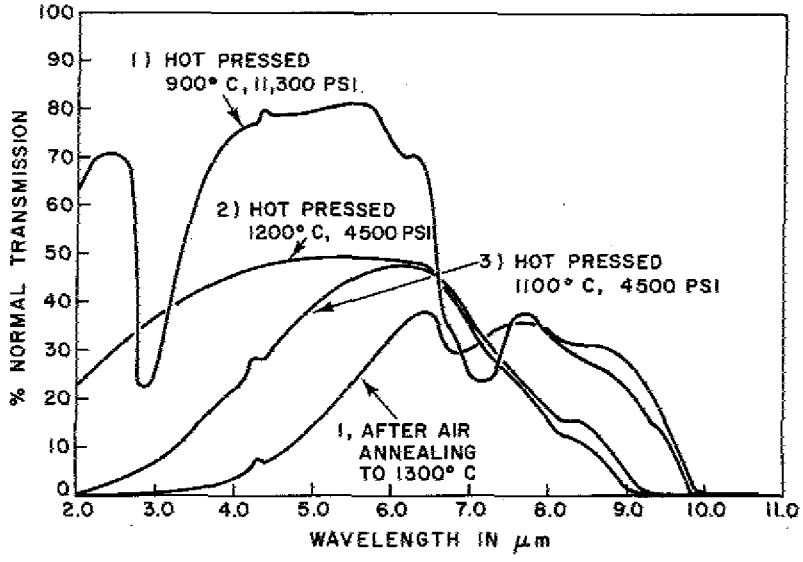


(a) Specimens made by author. Note: (LiF) means that the specimen was hot-pressed with LiF.



(b) JPL high-purity specimens as-hot-pressed by M. Leipold. While these specimens do not necessarily represent the optimum transparency achieved, they show the characteristic absorption bands.

Fig. 14 - Typical ir transmission of as-hot-pressed MgO. Note large absorption bands with the lowest pressing temperature and highest pressure. These are not present when pressing is at 1100°C with lower pressure, but overall transmission is substantially reduced. Transmission

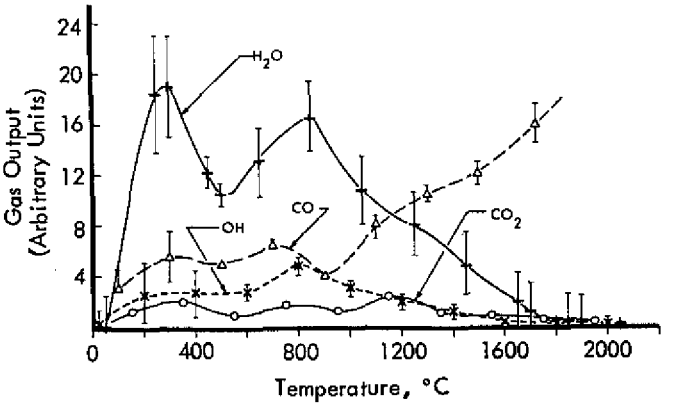


(c) Cornell MgO pressure sintered by P. Morgan

Fig. 14 (Continued) - Typical ir transmission of as-hot-pressed MgO. Note large absorption bands with the lowest pressing temperature and highest pressure. These are not present when pressing is at 1100°C with lower pressure, but overall transmission is substantially reduced. Transmission increases some with further increase in pressing temperature (1200°C) as normal MgO pressing conditions are approached. Note the elimination of the absorption band at 2.8 μm on annealing the sample pressed at 900°C, but not of other bands and the substantial reduction in transparency. These annealing results are essentially identical to those at 1150°C.

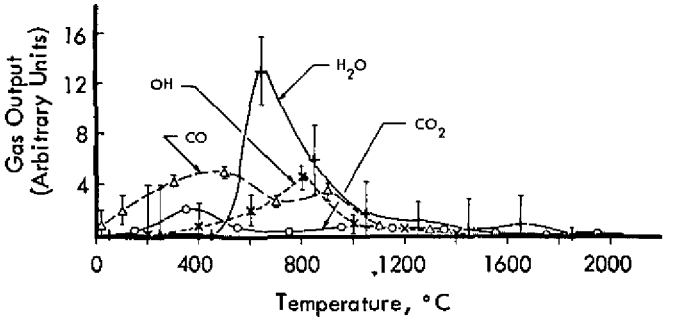
often varied substantially. The most pronounced variation in bands with fabrication parameters was the generally increasing intensity of the band centered about 2.75 microns with lower pressing temperature. For example, M MgO pressed without additives and C MgO pressed at 1100°C showed no absorption at 2.75 microns, but M MgO pressed at about 1000°C with LiF showed some absorption there and C MgO hot-pressed at 900°C had strong absorption at 2.75 microns. The latter also had a fairly strong absorption band at about 7 microns. Specimens hot-pressed from FH powder calcined in air had an absorption band at 6.1 microns and showed no transmission beyond 6.8 microns. Similar results were observed with specimens made from calcined MBC powders. The band between 8.0 and 8.3 microns in F MgO was generally larger when the band at 7 microns was smaller.

Infrared absorption bands at about 2.8 and 4 microns were eliminated in specimens about 0.1 in. thick after annealing to 1100°C or less regardless of the type of MgO or method of hot-pressing used (with or without LiF). Similarly, the absorption band around 7 microns was eliminated from specimens about 0.1 in. thick after annealing to temperatures of about 1100°C whether they were made with or without LiF. The band in F MgO between 8.0 and 8.3 microns tended to shift to longer wavelengths with annealing and it



(a) Tested as hot-pressed

× Mass Number 17: OH
+ Mass Number 18: H_2O
△ Mass Number 28: CO
○ Mass Number 44: CO_2

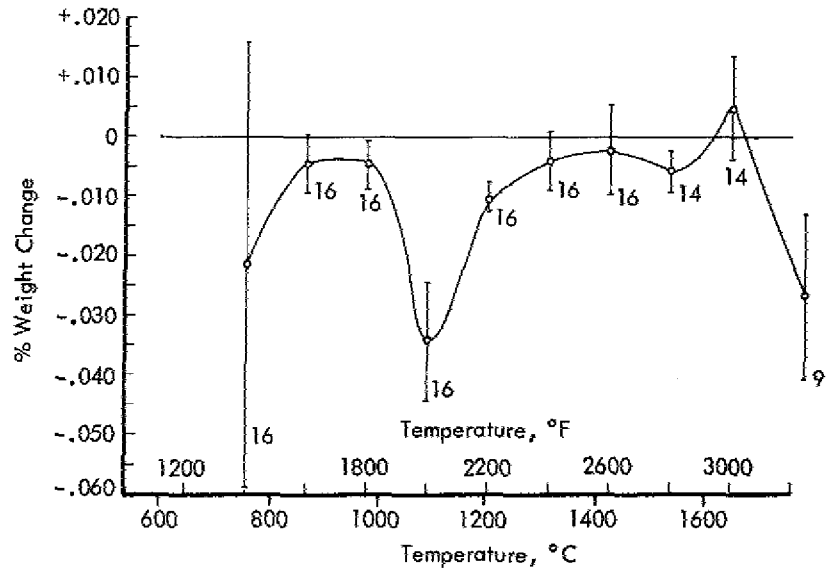


(b) Tested after air annealing first to 900° F (485° C) slowly, then rapid annealing for 1.5 hours to 3100° F (1705° C)

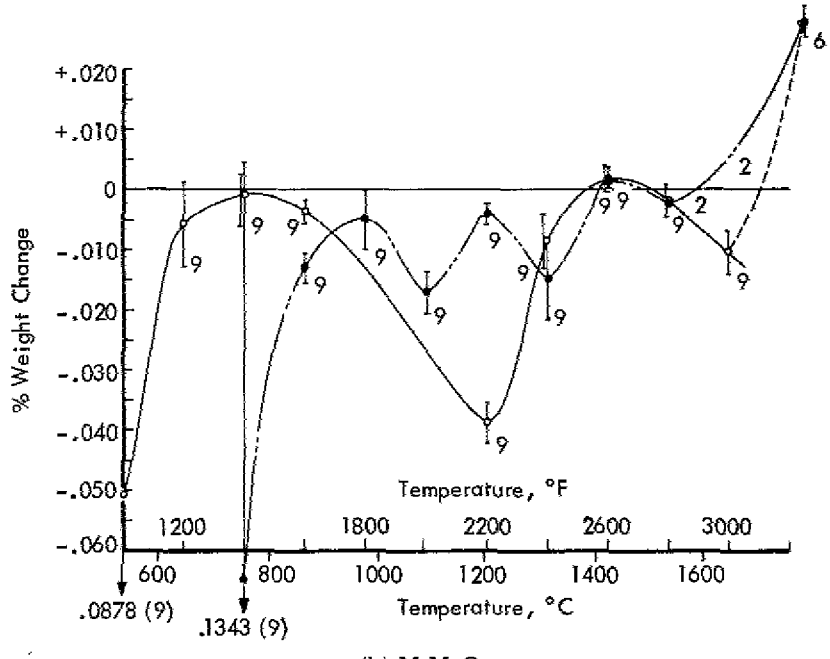
Fig. 15 - Mass spectrometer Knudsen cell analysis of outgassing from dense hot-pressed F MgO. Data represent net outgassing (background subtracted—vertical bars represent range of background variation). The specimens are from the same hot-pressed disk.

high-temperature annealing (Fig. 15). (A single crystal of MgO showed no significant outgassing.) Specimens run in the mass spectrometer frequently "blistered" due to the above impurity outgassing. Volatilization of MgO as indicated by the appearance of mass 24 (Mg) was only faintly indicated above about 1900° C.

These results are corroborated by weight losses shown both in the mass spectrometer tests and in numerous other (slower) annealing. A sequential series of the latter (including



(a) F MgO



(b) M MgO

Fig. 16 - Weight loss on annealing dense MgO hot-pressed without additives. Points represent actual weight lost at each temperature, not cumulative weight loss. Vertical

Table 5
Annealing Weight Loss of Mallinckrodt MgO + LiF

Composition	Total Percent Weight Loss of Bars Approximately 1 by 0.25 by 0.08 in. After:				
	1650°F (900°C)* 1 Hour	1750°F (955°C)* 1 Hour	2000°F (1095°C) 4.5 Hours	2400°F (1315°C) 1 Hour	2600°F (1425°C) 1 Hour
MgO	1.18	1.26	—	—	—
	1.05	1.09	—	—	—
	1.23	1.29	—	0.95	0.27
	0.63	0.67	—	1.01	1.89
	0.59	0.63	—	0.67	1.49
	0.98	1.18	—	1.82	
Average	0.94	1.02	—	1.11	1.22
Standard deviation	0.25	0.27	—	0.43	0.67
Number of specimens	6	6	—	4	3
MgO-1 w/o Al_2O_3	0.68	0.72	0.36	—	—
	0.70	0.75	1.62	—	—
	1.92	2.01	1.59	—	—
			1.30		
			1.01		
			1.45		
			1.22		
			1.56		
			1.23		
			1.62		
Average	1.10	1.16	1.30	—	—
Standard deviation	0.7	0.7	0.36	—	—
Number of specimens	3	3	10	—	—

*Subsequent firing of same bars, all other data for single firing of separate specimens.

those black as-hot-pressed, or those from calcined MBC, showed much higher weight losses, sometimes approximately 10%. Weight losses in mass spectrometer analysis generally increased with the amount of outgassing.

DISCUSSION

Occurrence of "Gaseous Impurities"

All of the ir absorption bands found in MgO have been previously shown by the author (26) to occur in dense hot-pressed CaO. Most were identified as follows: hydroxide (2.75 microns), carbonate (7 microns), and probably bicarbonates (about 4 and 6 microns). The indicated inverse relationship between the carbonate and 8.0 to 8.3-micron bands and the shift of the latter again suggest that the carbonate band may be the cause of the longer wavelength band, possibly by partial decomposition or solution of the carbonate. These identifications are corroborated by the mass spectrometer data showing H_2O, CO_2, and related species being given off. The high-temperature output of CO appears somewhat high for just decomposition of CO_2, indicating that some complex of CO may be contained in the solid as suggested from the ir data. The greater relative presence of H_2O and OH shown by the mass spectrometer than by ir analysis is due to the greater overall sensitivity of the former, and probably to less sensitivity of the ir for OH^- than for CO_3^{2-} radicals.

The outgassing observed to quite high temperatures may be due partly to faster heating and partly to the use of solid samples in the mass spectrometer. However, both the mass spectrometer powder data (10) and ir data on solid samples with much slower annealing also show outgassing to surprisingly high temperatures. Leipold and Nielsen (29) have reported H_2O still being evolved from MgO to temperatures of at least 2100°C. They (29) and Freund (30) have suggested reasons for such stability.

It may seem a surprise to many that carbonates and hydroxides, which are normally considered readily decomposed, could be left in dense hot-pressed bodies. However, it must first be remembered that they are left in only small amounts (0.1% or less on a weight basis). Second, it should be noted that hot-pressed MgO bodies have often reached 80 to 100% of their theoretical density in the temperature range of 800° to 1100°C; therefore, the combination of limited porosity and its fine nature (due to the fineness of the powders used) makes diffusion of any gases out of the powder much slower (26). In conjunction with this, it should be recalled that though substantial decomposition may occur at relatively low temperatures, much higher temperatures are often required to eliminate the last traces of decomposition gases (31). For example, $Mg(OH)_2$ loses about 98% of its water at about 400°C but still contains about 0.3% after heating to 700°C (32), even in the very loose packed condition common for calcining.

Another factor in the retention of carbonates and hydroxides may be stabilization under pressure. The author has previously noted (26) that geological data such as that of Wyllie (33) show that under mechanical pressures of 1000 psi or less $Ca(OH)_2$ and $CaCO_3$ will melt rather than decompose and form binary and ternary eutectics with CaO. Since Ca is an impurity (Table 3), it may form carbonates and hydroxides thus contributing to their retention. A similar study of the MgO-CO_2-H_2O system by Wyllie and Tuttle (34) reports that such stabilization does not occur in this system, but whether their results are accurate to a fraction or a few percent is unknown. However, more recent work by van Velden

The majority, and probably all, of such hydroxide and carbonate impurities must be from the powder itself and not from contamination by or reaction with the graphite die. First, the powders have substantial "ignition" losses and show higher levels of H_2O, CO_2, etc., outgassing in the mass spectrometer (10). Second, these impurities were observed by Carnall (37), (who first pointed out the correct identification of the ir bands to the author), using the same and other powders with or without LiF in metal dies. They have also been reported in otherwise very-high-purity MgO made by Leipold and Nielsen (38). The author has also observed these bands in their F and high-purity MgO (hot-pressed in nongraphite dies, Fig. 14b) and in C MgO hot-pressed directly from the hydroxide (23).

The powders probably acquire these impurities in one of three ways. First, some may be left from incomplete reduction of the starting compound, especially where low calcining for fine particle size is used. Second, some re-reaction as indicated in experiments of Wyllie and Tuttle (as reported by Langmuir (39)) may occur on cooling from calcining since all of the released CO_2 and H_2O is probably not able to diffuse out of the powder, especially in large or more densely packed loads. Third, some of the gas is acquired from the atmosphere as shown in preceding work (10) and in particular Ref. 40. Such atmospheric contamination need not be simple physical adsorption but may involve formation of stable compounds as suggested by the occurrence of a high-temperature reaction in the second DTA run in preceding work (10). Webster, Jones, and Anderson (41) have shown that such changes can occur when water is absorbed on MgO. Further, Chown and Deacon indicate that MgO can react with CO_2 in the presence of water vapor (42).

Effects of Gaseous Impurities During Annealing

Blistering and bloating are clearly a result of pressure developing in the bodies during annealing due to evolution of CO_2 and H_2O. The limited quantities of such impurities can have such gross effects because the decomposition of the previously solid carbonates results in about a 10,000-fold expansion of the gaseous products. The occurrence of clouding and associated grain boundary porosity only during the first annealing to 800° to 1200°C in some specimens, especially with more rapid firing, shows that clouding is a manifestation of the porosity which is caused by the gaseous impurities.

There is thus a complete spectrum of effects of gaseous impurities, ranging from no obvious effect (at least in some thinner specimens) through progressive degrees of clouding, blistering, and bloating. These in general represent an increasing concentration of gaseous impurities, roughly in the order listed. However, considerable variation occurs probably resulting from local concentrations of such impurities which would only partially be reflected in the specimen-to-specimen variations in the various analyses used. While some inhomogeneous clouding and blistering is clearly related to mechanical variations in samples (e.g., interfaces left from previous successive cold pressings), the frequency of these in specimens that appeared homogeneous as-hot-pressed clearly indicates inhomogeneous distribution of these impurities. Such inhomogeneity may result, at least partially, from the inhomogeneously distributed Ca-impurity content being present as the hydroxide, carbonate, and possibly bicarbonate. Laminar-shaped bubbles and explosions previously noted in hot-pressing (10) are thus progressively more extreme demonstrations of such impurities.

Decomposition of the carbonates does not proceed catastrophically on annealing be-

it proceeds slowly enough, resultant gases can probably diffuse along grain boundaries, leaving behind at most very fine grain boundary porosity that can be removed by sintering. Thus, bodies with limited quantities of gaseous impurities can become transparent, or retain and improve transparency during firing as observed. However, in thick specimens, diffusion paths from the center are too long, so greater units of impurity or gas are retained, giving the central opaque regions or bloating observed. Higher concentrations (locally or generally) of these impurities also lead to greater problems, but voids left from hot-pressing could also be important since decomposition would not be inhibited at the void (at least not until substantial gas pressure is achieved in the void). For example, the author has previously shown fracturing of a large body apparently originating from a small void through such pressurization (11,12). Miles et al. (43) have recently reported that gas is released from hot-pressed MgO bodies that were fractured in a vacuum. This probably results from such pressurization. However, pressure in voids is limited not only by pressure-size and pressure-decomposition relations but also probably by some re-reaction of constituents (e.g., MgO and CO_2) on cooling, as pointed out by Langmuir (39).

The much greater differentiation of specimens, from different lots, after annealing than after hot-pressing is then quite understandable in view of the much greater stabilization of gaseous impurities in hot-pressing than in annealing and their pronounced increase in volume on decomposition. The sensitivity of annealing results to these impurities and to their state makes this an important detector for these variations. The lack of clear effects of moisture exposure suggests carbonates or bicarbonates are the major problem.

The variety of materials and conditions investigated here shows that this problem of gaseous impurities is quite prevalent and basic. This is further shown by results of other investigators (9,43-45) including those based on pressing in other metal or ceramic dies. Considering the prevalence of this problem, and the difficulty of ascertaining which specimens will cloud and which will not, a long slow anneal of present hot-pressed MgO bodies prior to any other elevated temperature exposure is generally recommended.

Loss of Other Impurities and Additives

Black, dull hot-pressed specimens, which are usually colored by traces of C or graphite, become white or colorless, depending on opacity or translucency, indicating that this material is readily lost on annealing.

Since the Na content of M MgO can readily be reduced substantially below reported starting levels, even with the addition of 2-w/o NaF, Na and possibly other alkali metals are probably lost from bodies made without LiF or NaF. This is corroborated by work of Chung et al. (17), who showed that K and Na contents of reagent-grade MgO powders decreased from about 0.5% to 0.3% during similar hot-pressing without additives. The mechanism of such losses is not readily understood nor have cursory investigations with the mass spectrometer been enlightening; however, reaction with or some association with carbonate impurities may be an important factor.

The substantial difference between Li (or Na) and F contents after hot-pressing or annealing shows that some reaction of F and MgO or related impurities has occurred. Such reactions have been reported by Ludekens et al. (46) in dry-powder mixtures in the range of 500° to 800°C. They report that complete anion exchange occurs between LiF and MgO or CaO as well as NaF-CaO, while NaF forms a mixed fluoride, $NaMgF_3$, with MgO.

Surface and Interior Changes

Grain growth is substantially reduced by porosity in agreement with Spriggs et al. (49), although they did not observe grain growth as high as reported here. This is attributed at least partially to introducing some porosity in their specimens, as shown by clouding (45) from carbonates apparently due to a faster annealing cycle. The smaller surface grain size observed in many machined specimens at lower temperatures is attributed to inhibition of grain growth in the surface by the high density of dislocations introduced by machining as discussed elsewhere (13,50). Surface limitations on grain growth and impurity effects may also contribute to limiting surface grain size in annealed bodies. The variable distribution of impurities and loss of some from the surface are probably factors in the occurrence of larger surface grains in areas of some bodies annealed at high temperatures.

Na apparently inhibits grain growth since it is lost from the surface of specimens made with NaF which have larger surface grains. Loss of Na may also be the cause of grain growth changes of M MgO made without additives (and possible with LiF, see Fig. 6) since this material has substantial Na content which is reduced on annealing. This change also generally corresponds with the maximum blackening of M MgO, suggesting a relationship.

Another important surface change is the marked increase in surface hydration of annealed F MgO. This could be caused by calcium being present in the as-hot-pressed condition as a hydroxide or carbonate which would not hydrate, but on annealing, these could break down on the surface, leaving free CaO which would hydrate. Removal of this CaO by chemical polishing, or diffusion at higher temperatures, would stop the hydration as observed. The fact that this hydration does not occur with other MgO bodies shows the importance of not only the type of impurity present but also its physical or chemical association with the matrix or other impurities. The difference in structure of surface Ca- and Si-rich bodies (F and M MgO) further demonstrates the importance of impurity association. The occurrence of whiskers at grain boundaries in replicas of F MgO indicate some free CaO is present since similar whiskers are observed in CaO (10), but not other MgO bodies.

Since many specimens were vacuum-hot-pressed and since Rossi and Fulrath (51) note that pores cannot be trapped in grains unless they contain gases, the observed entrapped porosity is further evidence of gaseous impurities.

The changes in color of a given body indicate changes in impurity state or distribution. For example, F MgO (made without LiF or NaF) acquires a brown-orange color which may be due to iron oxide changing valence or distribution (e.g., solution versus precipitation). Differences in color between bodies made from the same raw material, but with or without fluoride additives, indicate that additives interact with impurities. For example, the above F MgO does not acquire a brown-orange color if made with LiF.

The above changes must be considered when evaluating mechanical properties of such bodies, as will be done in a subsequent paper on MgO (1).

SUMMARY AND CONCLUSIONS

Clouding, bloating, and blistering of dense, translucent-transparent hot-pressed MgO made with or without additives were often found to be major problems during subsequent annealing. These problems could be minimized by a very slow heating rate (approximately

Grain size was higher with LiF and intermediate with NaF (but with a mixed-grain structure) compared to annealing of specimens without additives, while porous specimens gave the finest grain size. Residual porosity from incomplete densification or clouding is generally fine and located at grain boundaries usually on triple lines, until annealed to temperatures of 1400° to 1500°C. Above these temperatures, pores are generally larger and usually within the grains approximately in the shape of negative crystals.

Ca and Si impurities were most common, generally located together in grain boundary regions but varying substantially in content from specimen to specimen and within a given specimen. At finer grain sizes, random patches a few to several grains in size occurred. However, after annealing to or above 1400° to 1500°C, these were predominantly along triple lines with some random patches on grain boundary surfaces much smaller than the grain size. There was some tendency for a higher concentration of Ca near the surface.

Surface scratches showed substantial rounding or elimination on slow annealing to 1100° to 1200°C and were well rounded or gone after annealing to 1200° to 1400°C. Above 1400° to 1500°C, Ca- and Si-rich structures formed on annealed surfaces. These surface structures formed in characteristic shapes, e.g., rectangular protrusions, on bodies of MgO from certain raw materials.

Changes in color on annealing indicate that impurities are changing valence or chemical association. Differences in color between bodies from different powder sources show variation in impurity content or association between similar powders. Important differences, such as surface hydration after annealing in some bodies, indicate the importance of the physical or chemical association of a given impurity such as Ca.

Na and Li from NaF or LiF additives are primarily lost during hot-pressing, with the last traces of Li being lost by annealing specimens about 0.1 in. thick to about 1100°C. Na impurities also are further reduced by annealing. More F remains than Li or Na, probably due to the formation of MgF_2 or $NaMgF_3$. However, F contents can be reduced to a few hundred parts per million content in specimens about 0.1 in. thick by annealing to 1300° to 1500°C.

ACKNOWLEDGMENTS

The author gratefully acknowledges the assistance of A Donovan in preparing test specimens and determining weight losses; A Jenkins and G. Way for optical photography; C. Smith for electron microscopy; R. Racus for electron probe analysis; R. Evans, B. Illi, and K. Halderson for ir measurements; H. Goldberg for mass spectrometer analysis; V. Eggebraaten for fluoride analysis; and K. Halderson for lithium and sodium analysis. The aid of C. Burns and Dr. P. Becher in editing the manuscript was also most helpful.

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